



## Second-generation green diesel from castor oil: Development of a new and efficient continuous-production process



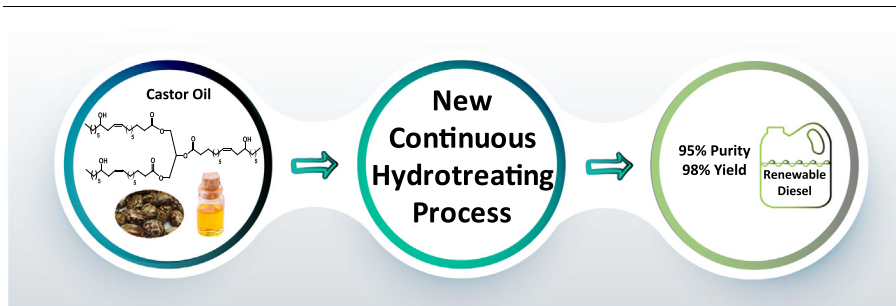
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### HIGHLIGHTS

- Green diesel was obtained in 95.3% purity and 98.4% relative yield.
- Secondary reactions of castor oil were suppressed using two-stage continuous system.
- Green diesel met most of specifications of European standard EN 590.
- Green diesel blend with petro-diesel met specifications for CFPP of diesel grade B.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A new continuous process for the selective production of castor-oil green diesel was developed, leading to 95.3% purity and ca. 98% relative yield. Castor oil was hydrotreated in fixed-bed continuous reactors, with one or two stages, using NiMo/Al<sub>2</sub>O<sub>3</sub> as catalyst. It was demonstrated that performing the process in a single hydrotreating bed the presence of hydroxyl groups in castor oil afforded secondary reactions that led to low values of purity and yield. Running the reactions in a two-stage continuous system allowed to remove, in the first bed at 270 °C, hydroxyl groups and unsaturations before the deoxygenation of the carboxylic groups in the second bed at 350 °C, improving in this way the purity and the yield considerably. Physicochemical properties of the so-obtained product met most of the specifications of the European standard EN 590 but the CFPP. Blending of green diesel (20% vol) with petro-diesel satisfied CFPP specifications for diesel grade B.

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## 1. Introduction

Because of the threats of global climate change, a renewed interest in researching biofuels has been increasing in last decades [1]. Biodiesel has been considered as a suitable substitute for petro-diesel since it has good cetane number and lubricity together to biodegradability and non-toxicity [2]. However, biodiesel also presents problems of chemical stability, cold flow, low calorific power, incompatibility with some engines and filterability (hazes)

due to the presence of oxygen in its structure [3,4]. This has encouraged the development of green diesel from vegetable oils or animal fats by hydroprocessing, in which oxygen is eliminated either as water, carbon dioxide or carbon monoxide [4–11]. It has been demonstrated that green diesel has total compatibility with petro-diesel, high calorific value (44 MJ/kg), low specific gravity (0.78), excellent storage stability, and very low combustion emissions [12]. In comparison with petro-diesel, green diesel has between 66–84% and 41–85% savings for fossil and greenhouse gas emissions, respectively [12].

Supported metal-sulfide catalysts are widely used in hydrotreating and hydrocracking applications for removing sulfur

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and nitrogen from petroleum fractions [13]. Therefore, these catalysts are used at industrial scale for deoxygenation of triglycerides, most common being sulfided NiMo or CoMo supported on  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  [13,14]. Palm oil has been hydrotreated with sulfided NiMo/ $\gamma$ - $\text{Al}_2\text{O}_3$  in a continuous-flow fixed-bed microreactor at 300 °C, 3–8 MPa  $\text{H}_2$ , 1–2  $\text{h}^{-1}$  LHSV and  $\text{H}_2/\text{oil}$  volume ratio of 750–1000 N ( $\text{cm}^3/\text{cm}^3$ ), affording a product yield of 90.0% and n-alkane purity higher than 95.5% [6]. On the other hand, soybean-oil hydrotreating has been evaluated over various supported catalysts in batch reactors at 9.2 MPa  $\text{H}_2$ , 400 °C and 2 h reaction [15]. The hydroprocessing conversion order was: sulfided NiMo/ $\gamma$ - $\text{Al}_2\text{O}_3$  (92.9%) > 4.29 wt% Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  (91.9%) > sulfided CoMo/ $\gamma$ - $\text{Al}_2\text{O}_3$  (78.9%) > 57.6 wt% Ni/ $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  (60.8%) > 4.95 wt% Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$  (50.8%) > 3.06 wt% Ru/ $\text{Al}_2\text{O}_3$  (39.7%) at a catalyst/oil weight ratio of 0.044. From all these studies it has been concluded that the best catalyst for oxygen removal in fats and oils is sulfided NiMo/ $\text{Al}_2\text{O}_3$ .

First generation biofuels include those obtained from food crops such as palm oil, rapeseed oil, or soybean oil. Alternatively, second generation biofuels are based on residual biomass, such as wood/forestry residues or waste cooking oil, as well as non-edible oils, i.e. castor oil or jatropha oil [16]. Non-edible energy crops such as jatropha or castor oil do not compete directly with food uses, and they grow under non-very stringent conditions [16,17]. Castor oil has unique physical and chemical properties, since it is composed mainly of ricinoleic acid triglycerides (ca. 90%), that bear hydroxyl groups near to unsaturations. Due to these hydroxyl groups, biodiesel obtained from castor oil presents problems for meeting specific gravity and viscosity specification of the European standards [18]. Thus, substantial changes in the structure of castor oil have to be carried out for producing suitable fuels [19]. A limited number of papers have reported the hydrotreating of castor oil or its derivatives for obtaining biofuels [20–22]. Meller et al. reported deoxygenation of methyl esters of castor oil in a batch reactor with Pd/C, at 2.5 MPa  $\text{H}_2$ , 340 °C and 6 h, using hexane at supercritical conditions. The product was composed of 87 wt% heptadecane and 9 wt% octadecane with higher than 95% yield [20]. A recent study reported the conversion of several vegetable oils to diesel and jet fuels (deoxygenation and cracking products) with Pt/ $\text{Al}_2\text{O}_3$ /SAPO-11 in a trickle bed reactor at 370–385 °C, 3 MPa  $\text{H}_2$  and 1  $\text{h}^{-1}$  LHSV [21]. Specifically, the lowest product yield (78.2 wt%) was obtained with castor, compared to the yields obtained with the other oils (82–85 wt%). In addition, aromatic compounds in the products obtained from soybean, sunflower and camelina oils ranged from 14.8 to 15.5% while aromatic compounds from hydrotreating of palm oil, tallow and castor oil ranged from 1 to 2%. In another study, Liu et al. reported the production of bio-aviation biofuel from hydroprocessing of castor oil in a continuous-flow fixed-bed microreactor at 300 °C, 3 MPa, 2  $\text{h}^{-1}$  WHSV and 160 ml/min  $\text{H}_2$ , using bifunctional catalysts with different acid strength [22]. Highest aviation-range alkane yields (91.6 wt%) with isomer/n-alkane ratio of 4.4–7.2 were achieved over Ni supported on acidic zeolites.

In these previous papers reporting the hydrotreating of castor oil the term “yield” is ambiguous and it seems that it was mistaken for “purity”. As it will be discussed later, maximum theoretical yields for castor oil hydrotreating are in the range 78–82%, and these papers reported yields higher than these values. Moreover, the effects of process variables as well as the applicability as a fuel of hydrotreated products from castor oil have not been addressed, so far. To the best of our knowledge, there are not reports on the selective production of green diesel from castor oil in continuous flow. Previous reports have investigated the production of fuels from castor oil via deoxygenation and cracking reactions using as catalysts Pt/ $\text{Al}_2\text{O}_3$ /SAPO-11 and Ni/H-zeolites.

Recently in our group, castor oil was hydrotreated in a batch system using Ni-Mo catalysts supported on  $\gamma$ - $\text{Al}_2\text{O}_3$  [23]. The best

result was obtained at 350 °C and 9 MPa with the catalyst containing 4.5% NiO and 20%  $\text{MoO}_3$ , leading to ca. 82% yield to green diesel and 100% conversion, as well as 54.4% and 20.9% selectivities to C17 and C18 alkanes, respectively. Considering the potential of castor oil in a commercial application, new insights are presented in this study focusing in a continuous process. In this paper, castor oil was hydrotreated in a continuous-flow fixed-bed microreactor using a commercial sulfided NiMo/ $\text{Al}_2\text{O}_3$  to selectively obtain green diesel, without promoting cracking reactions. The reactions were conducted in one or two stages using two catalytic beds in series. The effects of process variables on the purity and the yield of products were evaluated. The applicability of the obtained product as a diesel fuel was determined under standardized methods. Moreover, green diesel was blended with petro-diesel for improving cold flow properties.

## 2. Materials and methods

### 2.1. Materials

Technical grade castor oil (acid value, 1.96 mg KOH/g) and palm oil (acid value, 0.25 mg KOH/g) were purchased from a local distributor. The composition in fatty acids of these oils is shown in the Table 1.  $\text{H}_2$  (99.99%) was supplied by Linde Group, Colombia. NiMo/ $\text{Al}_2\text{O}_3$  catalyst (Katalco 61-1T, composed of 3.5% NiO and 10.5%  $\text{MoO}_3$ ) was obtained from Johnson Matthey, USA. Surface area (BET), pore volume and pore size of this catalyst were respectively 262  $\text{m}^2/\text{g}$ , 0.67  $\text{cm}^3/\text{g}$  and 8.3 nm.

### 2.2. Ex-situ pre-sulfiding of NiMo/ $\text{Al}_2\text{O}_3$

The procedure of pre-sulfiding was adapted from the work of Sanchez et al. [23]. NiMo/ $\text{Al}_2\text{O}_3$  (50 g) was crushed and sieved to 20–40 mesh before blending with hexadecane (85 g) and elemental sulfur (5 g). This blend was introduced in a 250 mL-high pressure batch reactor (Parr Instruments). The system was purged and pressurized with 9 MPa  $\text{H}_2$  before heating to 300 °C. The temperature (300 °C) and agitation (350 rpm) were kept constant for 1 h. Before hydrotreating experiments the catalyst was washed with dichloromethane. Then, the solvent was evacuated under reduced pressure.

### 2.3. Hydrotreating of castor oil

The experiments were conducted in a continuous-flow system with two fixed-bed reactors in series (0.9 cm ID), as shown in Fig. 1. Two kinds of experiments were conducted: a) experiments with a single bed, where only one reactor was packed with catalyst, and b) experiments with two beds, where both reactors were packed with catalyst. In both cases, the pre-sulfided NiMo/ $\text{Al}_2\text{O}_3$  was used as the catalyst. The catalyst was crushed and sieved with

**Table 1**  
Fatty acid profile of castor oil and palm oil.

Fatty acid	Composition (w/w%)	
	Castor oil	Palm oil
Lauric	0.00	0.22
Miristic	0.00	1.01
Palmitic	0.91	43.3
Stearic	1.03	4.52
Oleic	7.42	40.61
Linoleic	3.10	9.22
Linolenic	0.00	0.17
Ricinoleic	87.0	0.00

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